



⑪ Publication number: **0 526 101 A1**

⑫ **EUROPEAN PATENT APPLICATION**

⑳ Application number: **92306733.4**

⑤① Int. Cl.⁵: **B01J 31/12, C07C 6/04,
C07C 11/06**

㉔ Date of filing: **23.07.92**

③① Priority: **30.07.91 FI 913627**

④③ Date of publication of application:
03.02.93 Bulletin 93/05

⑧④ Designated Contracting States:
**AT BE CH DE DK ES FR GB GR IT LI LU MC NL
PT SE**

⑦① Applicant: **NESTE OY**
Keilaniemi
SF-02150 Espoo (FI)

⑦② Inventor: **Hietala, Jukka**
Luhtitie 2 B 5
SF-06400 Porvoo (FI)
Inventor: **Knuuttila, Pekka**
Torpparintie 4
SF-06400 Porvoo (FI)
Inventor: **Leskela, Markku**
Koivusyrjä 25 I
SF-02130 Espoo (FI)
Inventor: **Sillanpää, Reijo**
Auskultantinkatu 9
SF-20780 Kaarina (FI)
Inventor: **Lehtonen, Ari**
Frantsinkatu 5 A 29
SF-20380 Turku (FI)

⑦④ Representative: **Lamb, John Baxter et al**
MARKS & CLERK 57-60 Lincoln's Inn Fields
London WC2A 3LS (GB)

⑤④ **Metathesis catalyst and its preparation and use.**

⑤⑦ The invention relates to a catalyst for use in the metathesis reactions of olefines, characterized in that it comprises an after-treated wolfram complex, which contains diol ligands and hydrocarbon ligands, which latter are benzenes substituted with a lower alkyl group.

EP 0 526 101 A1

The present invention relates to a catalyst to be utilized in the metathesis reactions of olefines as well as a method for preparing it.

Furthermore, the invention relates to metathesis process for the conversion of olefines into olefines having a different molecular weight.

The metathesis, or in other words the disproportionation, of olefines relates to a reaction, wherein one or more olefines are converted into olefines having a different molecular weight. An olefine may be disproportionated with itself into an olefine having a higher molecular weight and into an olefine having a lower molecular weight. In this case, the reaction may be called "self-disproportionation". Two different olefines may also be converted into other olefines by means of the metathesis reaction.

In order to function, the metathesis reactions of olefines require a catalyst system, which includes a transition metal compound, often a cocatalyst and sometimes also a compound acting as a promoter. The catalyst systems based on wolfram or molybdenum are especially efficient. Such catalysts generally comprise a wolfram or molybdenum oxide on an inorganic carrier, which is e.g. silica or alumina. It is known to add to such catalysts different substances as a promoter. Thus, e.g. according to the EP publication 152 112, titanium oxide or other titanium-containing substances are added to the surface of the catalyst as a promoter. According to the US patent 4 559 320, it is known to use a wolfram catalyst on a silica carrier, into which magnesium oxide is additionally mixed. According to the EP publication 50 013, a catalyst composition is known comprising a molybdenum oxide or a wolfram oxide on a silica carrier.

According to the US patent 3 956 178, a metathesis catalyst of three components is known, which catalyst is prepared from a wolfram compound, an organic ligand and an organo-metallic compound. In this patent, the wolfram compound is a wolfram oxychloride and the organic ligand contains a nitrile or ester group. As examples of ligands are mentioned phthalodinitrile, adiponitrile and ethyl phthalate.

According to the US patent 4 550 216, a metathesis catalyst is known, which comprises a compound between a wolfram, a halogen and a phenoxy group, which compound is possibly substituted.

The present invention comprises totally novel metathesis catalysts from organo-wolfram compounds. The inventive catalyst is mainly characterized in that it comprises an after-treated wolfram complex, which contains diol ligands and hydrocarbon ligands, which are benzenes substituted with a lower alkyl group.

The inventive method for preparing a catalyst is characterized in that

- a) a complex between an inorganic wolfram salt and a diol is formed,
- b) the complex obtained is caused to react with a benzyl anion or a benzyl anion substituted with a lower alkyl group for obtaining a wolfram complex containing diol ligands, benzyl ligands or benzyl ligands substituted with a lower alkyl group, and
- c) the wolfram complex obtained is impregnated into a carrier and calcinated.

The inventive metathesis process for the conversion of olefines, wherein the catalyst comprising a wolfram compound converts the olefine into olefines having a different molecular weight, is characterized in that said heterogenous catalyst comprises an after-treated wolfram complex, which contains diol ligands and unsubstituted benzyl ligands or benzyl ligands substituted with a lower alkyl group.

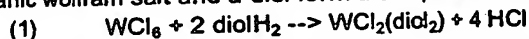
The preferred embodiments of the invention have the characteristics of the subclaims.

The wolfram complexes, in which as ligands are used a diol or a benzene substituted with a lower alkyl group, e.g. mesitylene, may be converted into heterogenous catalysts, which function in the metathesis of olefines at a higher activity than conventional catalysts, in which ammonium wolframate acts as a precursor. In addition, the preparation of the catalysts is easier, since the quantity of metal is low and the solubility in polar organic solvents is good.

The fact that the structures of the inventive synthesized precursors are of a novel type, is based on spectra and the determination of the released HCL. Thus, the inventive catalyst is used in the metathesis reaction, in which C=C bonds decompose and the moieties combine again. For example propene may be prepared from ethylene and 2-butene.

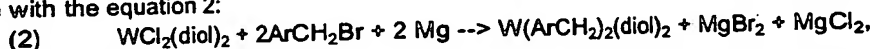
The inventive catalyst is prepared from a wolfram complex, in which as ligands are used diols and benzenes substituted with a lower alkyl group.

In the first step, an inorganic wolfram salt and a diol form a complex according to the equation 1:



in which diolH_2 = a diol compound, preferably a picanol or trans-1,2-cyclohexane diol.

Thereafter, the wolfram oxide obtained reacts with a bromide of a benzene substituted with a lower alkyl group, in this example with a mesitylene bromide, and a metallic magnesium for obtaining a catalyst precursor in accordance with the equation 2:



in which ArCH_2 is a mesitylene ligand.

The invention is next described by means of embodiment examples, which are not intended to limit the

invention.

The syntheses were made in a nitrogen atmosphere by using a Schlenck technique. The solvents, except for the tetrahydrofuran, were dried by calcium hydride and distilled, and the tetrahydrofuran was dried with a sodium-benzophenone mixture before the distillation. The diols were sublimated before use.

The hydrochloride released in the reactions was determined by bubbling the reaction solution with nitrogen and by passing the solution into an 0.10 M NaOH solution, which was titrated.

For the determination of the wolfram content and the chlorine content of the products, they were decomposed by means of a concentrated nitric acid. The chloride was potentiometrically nitrated and the wolfram was gravimetrically determined as an oxide. As for the catalysts, the wolfram was determined by means of XRF.

The infrared spectra were run in nujol (JASCO IR-810), the NMR spectra were run in carbon tetrachloride or deuteriochloroform (JEOL JNM-PMX 60, JEOL GSX-400).

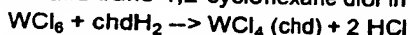
The catalysts were tested in a microreactor in a quartz-glass tube, through which passed the purified propylene (molecular sieves and copper catalyst). A sample of the gas flow passed through the catalyst was taken automatically at intervals of one hour and a gas chromatogram (column Chrompackin Fused Silica) was run.

EXAMPLES 1-3

A reaction of wolfram hexachloride with trans-1,2-cyclohexane diol

Example 1

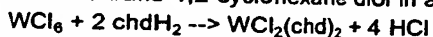
A reaction of wolfram hexachloride and trans-1,2-cyclohexane diol in a substance quantity ratio 1:1



1.635 g (4.12 mmol) of wolfram hexachloride was dissolved, when being in a Schlenk tube, in 15.0 ml of carbon tetrachloride. 0.4214 g (3.63 mmol) of trans-1,2-cyclohexane diol was added to the solution. The solution was admixed with a magnet mixer, and it was allowed to reflux for one hour. Thereafter, acid formation was no longer observed. The liquid phase was evaporated under an underpressure. The product was a black solid substance, which dissolved in 1,2-dimethoxy ethane and methanol. On the basis of an IR-spectrum, there was no organic moiety in the product. The test was repeated by using hexane as a solvent, whereby the product was similar to that obtained above.

Example 2

A reaction of wolfram hexachloride and trans-1,2-cyclohexane diol in a substance quantity ratio 1:2



1.276 g (3.22 mmol) of wolfram hexachloride and 0.7475 g (6.44 mmol) of trans-1,2-cyclohexane diol were dissolved in 15.0 ml of carbon tetrachloride. The solution was admixed and it was allowed to reflux for one and a half hour. Thereafter, acid formation was no longer observed. After the evaporation of the liquid phase, a red-brown substance was obtained, which dissolved well in toluene, chloroform, 1,2-dimethoxy ethane and methanol. It dissolved poorly in carbon tetrachloride, and it did not dissolve at all in hexane. From the compound were measured IR and ¹H NMR spectra (cf. Table 1). On the basis of these, the compound contains cyclohexane diolato groups bound to the wolfram.

69.6 mg of the cyclohexane compound of wolfram prepared was decomposed with 0.5 ml of concentrated nitric acid and 9.5 ml of water was added to the mixture. The released chloride ions were titrated potentiometrically by using a calomel and silver electrode. According to the determination, the compound contained 13.7% of chlorine.

For the determination of the wolfram, 102.2 mg of the compound prepared was admixed into 15.0 ml of concentrated nitric acid and 15.0 ml of water. The mixture was cooked for half an hour, whereafter a pale yellow WO₃ was separated by filtration. The wolfram oxide was dried by maintaining it at a temperature of 850°C for two hours. The oxide was weighed and according to the weight the quantity of wolfram obtained was 42.4%. If it is assumed that the four chloroligands of wolfram hexachloride are replaced with two biserrate cyclohexane diolato ligands, the WCl(chd)₂ thus obtained would contain 14.7% of chlorine and 38.1% of wolfram.

Example 3

A reaction of wolfram hexachloride and trans-1,2-cyclohexane diol in cold

1.899 g (4.79 mmol) of wolfram hexachloride was dissolved in 20.0 ml of 1,2-dimethoxy ethane, and 1.112 g (9.59 mmol) of trans-1,2-cyclohexane diol was added to the solution. The solution was maintained at a tem-

perature of -15°C and it was admixed by a magnet mixer. After mixing of five hours, no removal of the acid was observed. The solvent was evaporated under an underpressure. The product was a dark-brown, tough oily substance, which turned blue in connection with the sampling. The dark-blue colour possibly results from the reduction of the wolfram.

5

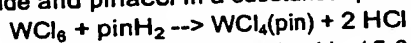
EXAMPLES 4 and 5

A reaction of wolfram hexachloride and pinacol

10

Example 4

A reaction of wolfram hexachloride and pinacol in a substance quantity ratio 1:1

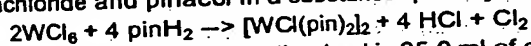


0.807 g (2.04 mmol) of wolfram hexachloride was dissolved in 15.0 ml of carbon tetrachloride. 0.2405 g (2.04 mmol) of pinacol was added to the solution, and it was allowed to reflux for two hours, after which no acid was removed. From a green solution was evaporated the liquid phase when subjected to an underpressure. The product was a green solid substance, which rapidly turned blue when coming into contact with air. The decomposition was very rapid, due to which IR- and ¹H NMR-spectra could not be measured from the compound. The green and blue colours relate to reduced wolfram compounds.

20

Example 5

A reaction of wolfram hexachloride and pinacol in a substance quantity ratio 1:2



1.600 g (4.04 mmol) of wolfram hexachloride was dissolved in 25.0 ml of carbon tetrachloride and 0.9645 g (8.16 mmol) of pinacol was added to the solution. All pinacol did not dissolve in this step. The reaction mixture was mixed with a magnet mixer, and it was allowed to reflux for four hours. After this, no acid formation could be observed. When the reaction advanced, the pale green solution turned dark blue. After the evaporation of the liquid phase, the product obtained was a strongly blue powdery substance. An IR-spectrum was measured from the product (cf. Table 1).

30

105.9 mg of the compound prepared was decomposed by mixing it in 0.5 ml of concentrated nitric acid. After this, 9.5 ml of water was added to the mixture, and the chloride content was determined. The content obtained was 7.6% (the calculated content was 7.7%).

35

40

45

50

55

Table 1 Characteristic IR absorptions and ^1H NMR spectra of alkoxo compounds of wolfram

5

10	Compound	Absorption peaks of IR spectrum (cm^{-1})	^1H NMR spectrum (δ /ppm)
15	$\text{WCl}_2(\text{chd})_2$	1040 C-O 1000 900-600 W-O	1.2 3.6 3.7
20	$\text{WOCl}_2(\text{chd})_2$	1040 C-O 1000 W=O 900-600 W-O	
25	$[\text{WCl}(\text{pin})_2]_2$	1140 C-O 960-620 W-O	
30	$\text{WOCl}_2(\text{pin})$	1140 C-O 980 W=O 960-600 W-O	
35	$\text{W}(\text{chd})_2(\text{mes})_2$		1.2 ; 1.8 2.2 ; 2.4 3.8 6.9
40	$\text{W}(\text{mes})_2(\text{pin})_2$	1160 C-O 960-900	2.3 ; 2.4 6.9

chd = cyclohexane diolato ligand

mes = mesitylene ligand

pin = pinacolato ligand

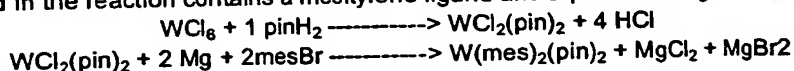
Example 6

Preparation of dimesitylene dipinacolato wolfram

0.613 g (1.55 mmol) of wolfram hexachloride was dissolved in 10.0 ml of toluene. 0.994 g (3.10 mmol) of tetrabutyl ammonium nitrate and 3.10 mmol of pinacol, dissolved in 15.0 ml of toluene, were added to the solution. The solution was mixed and it was allowed to reflux for six hours. As the reaction advanced, two liquid layers formed in the vessel, the lower one of which layers was an orange and the upper one was a yellow solvent. The orange solvent was dissolved in 10.0 ml of tetrahydrofurane, and 3.1 mmol (0.08 g) of magnesium and 3.1 mmol (0.47 ml) of bromine mesitylene were added to the solution. The solution was mixed at a temperature of 65°C for four hours. The solution was separated by decantation from

a non-reacting magnesium and the salt formed. The solvent was removed from the yellow solution by evaporating the solution under an under-pressure.

A ^1H NMR spectrum and an IR spectrum were measured from the brown yellow oily product (Table 1). The compound formed in the reaction contains a mesitylene ligand and a pinacolato ligand bound to the wolfram.



Preparation and testing of catalysts

The catalysts were prepared by separately impregnating each precursor (in one catalyst the diol was pinacol and in the other trans-1,2-cyclohexane diol) from THF into silica (PQ Corporation, CS-1231) and by calcinating with nitrogen at 600°C.

The catalysts were tested by passing propene through a catalyst bed at 400°C. A WHSV 4 h^{-1} conversion was observed in connection with both catalysts to be ca. 50%. (WHSV = weight hourly space velocity, i.e. 1 g of the feeding rate (g) flowing through the quantity of the catalyst per hour.) In the reference catalyst WO_3/SiO_2 , which contained the same quantity of wolfram (2%), the conversion was clearly below 50%. See Tables 2, 3 and 4.

Example 7

The sample was dimesitylene dipinacolato wolfram.

A ^{13}C -NMR and a ^1H -NMR was run from the sample with a 400 MHz device. The spectra may be fitted into the assumed structure.

The sample was known to dissolve in THF, due to which a catalyst impregnated from this solution was prepared, which catalyst contained 0.1294 g of the sample and 0.4450 g of silica. A calcination was performed in a nitrogen flux (ca. 10 l/h), 600°C, 1 h). During the calcination it was observed that a green and brown oil condensed in the reactor tube. It was allowed to react with propene, as shown in Table 2.

The wolfram content of an unused catalyst was 2.1% and after the reaction 2.5%.

Example 8

The sample was dimesitylene bis(cyclohexane diolato) wolfram.

0.29 g of the sample and 0.94 g of silica were impregnated. 0.5425 g of the catalyst was packed in the reactor and a calcination was performed with nitrogen (ca. 10 l/h, 600°C, 1 h). A brown greenish oil was observed during the calcination. It was allowed to react with propene, as shown in Table 3.

The wolfram content of an unused catalyst was 1.4% and the corresponding percentage after the reaction was 1.9%.

REFERENCE EXAMPLES 9-10

Two reference catalysts were prepared and tested. One of them is based on wolfram oxide chloride WOCl_4 , which is a wolfram complex dissolving in non-polar solvents, and the other one is based on a water-soluble salt $((\text{NH}_4)_2\text{WO}_4$, which is the most common reactant in metathesis catalysts.

Example 9

A reference catalyst from WOCl_4 , a low wolfram content

0.18 g of wolfram oxychloride was added gradually to and by simultaneously mixing with 1.28 g of silica in dichloromethane (0.6-1.6 mm, 310 m^2/g , The PQ Corporation). They were allowed to absorb at room temperature ca. for 3 hours, after which they were evaporated in a vacuum. The wolfram content was determined to be 2.3%.

0.5302 g of the catalyst was loaded into a reactor tube, calcinated with air at 600°C and flushed with nitrogen. It was tested in a metathesis reaction of propene at flows 1.0-6.0 l/h. The wolfram content after the run was 2.2%.

Example 10

A reference catalyst from $(\text{NH}_4)_2\text{WO}_4$, normal wolfram content.

A 3.9% water solution of ammonium wolfram 35.30 g was added gradually to and by simultaneously mixing with 19.96 g of silica (0.6-1.6 mm, 310 m²/g, The PQ Corporation). They were allowed to absorb at 80°C ca. for one hour, after which they were evaporated at 115°C for 17 hours.

16.7 g of the same solution was impregnated once again, it was allowed to absorb at 80°C and dried at 115°C for 23 hours. The metallic content was determined to be 5.8%.

0.3782 g of the catalyst was loaded into a reactor tube, calcinated with air at 600°C and bushed with nitrogen. It was tested in a metathesis reaction of propene at flows 0.1-4.1 l/h. The wolfram content after the run was 6.3%.

The test results are shown in the enclosed Tables 2-5. In the product distribution, the ratio between ethene and butenes is not the molar ratio 1:1 required by theory (the ratio of the weight percentages was ca. 1:2), since some ethene disappears from the system before the analysis. The conversion and the activity have been calculated from the butene observed.

EXAMPLE 7

TABLE 2

ACTIVITY OF A METATHESIS CATALYST

No. of run: Date: PRECURSOR: Carrier: Mass of catalyst (g): Area of catalyst (m ² /g): Molar mass of metal (g/mol): Content of metal (%): Temperature (°C): Activation: Propylene flow (l/h):									
L2 Feb 12-14, 1990 Dimethylsilene dipinacolato wolfram SiO ₂ Pq ca-1231 0.6-1.6 mm 0.3445 310 183.85 2.5 400 N2 ca. 10 l/h 600°C 1 h 1-6									
Time (h)	Ethylene (%)	Propylene (%)	Trans-2-butene (%)	1-butene (%)	Cis-2-butene (%)	Others (%)	Butenes (%)	Propylene conversion (g/gh)	Notes
0.0	11.968	44.553	14.058	6.673	10.667	12.071	31.408	51.4	82.5 propylene 1.0 l/h
1.0	9.008	48.017	16.137	3.918	14.128	6.792	36.183	53.1	85.2
2.0	8.632	47.618	17.600	4.371	13.646	8.133	36.617	52.9	84.9
3.0	8.655	47.136	17.239	4.603	13.403	8.764	35.265	52.9	84.9
4.0	8.307	47.424	17.282	4.663	13.401	8.923	35.346	52.8	84.8
5.0	8.361	47.489	17.337	4.634	13.427	8.752	35.398	52.8	84.8
6.0	8.195	47.515	17.344	4.556	13.440	8.950	35.340	52.7	84.7
7.0	8.089	47.620	17.374	4.530	13.485	8.902	35.389	52.7	84.6
8.0	8.769	47.548	17.402	4.346	13.503	8.432	35.251	52.7	84.6
9.0	8.625	47.670	17.434	4.371	13.559	8.341	35.364	52.7	84.6
10.0	8.341	47.402	17.375	4.504	13.482	8.896	35.361	52.8	84.8
11.0	8.519	47.363	17.391	4.408	13.496	8.823	35.295	52.8	84.8
12.0	8.484	47.609	17.524	4.407	13.575	8.401	35.506	52.8	84.8
13.0	8.352	47.728	17.626	4.215	13.740	8.339	35.581	52.8	84.8
14.0	8.391	47.816	17.711	4.198	13.758	8.146	35.647	52.8	84.8

TABLE 2 (continued)

TABLE 2 (continues)									
15.0	8.331	47.781	17.748	4.224	13.789	8.127	35.761	52.9	84.9
16.0	8.387	47.874	17.828	4.179	13.897	7.835	35.904	52.9	85.0
17.0	8.413	47.778	17.747	4.152	13.774	8.136	35.673	52.8	84.8
18.0	8.225	50.010	19.921	2.266	15.728	3.850	37.915	53.2	172.6
19.0	8.332	50.285	20.038	2.199	15.803	3.343	38.040	53.1	172.4
20.0	8.344	50.377	20.082	2.121	15.836	3.240	38.039	53.1	172.3
21.0	7.680	53.256	20.195	1.276	16.280	1.313	37.751	51.5	322.7
22.0	7.511	54.390	19.787	1.136	16.145	1.031	38.068	50.6	316.6
23.5	7.678	54.717	19.654	1.077	16.027	0.847	36.758	50.2	316.3
24.5	7.338	56.002	19.275	0.968	15.683	0.734	35.926	49.0	480.4
25.5	7.069	59.615	17.895	0.000	14.937	0.484	32.832	45.2	443.1
26.5	6.978	60.337	17.542	0.000	14.704	0.439	32.246	44.5	435.8
27.5	7.063	60.643	17.401	0.000	14.626	0.267	32.027	44.2	433.0
28.5	7.078	60.635	17.707	0.000	14.611	0.269	32.018	44.2	432.9
29.5	7.093	60.968	17.216	0.000	14.473	0.250	31.689	43.8	429.1
30.5	7.179	60.829	17.298	0.000	14.501	0.193	31.799	44.0	430.5
31.5	6.931	60.949	17.407	0.000	14.617	0.196	32.024	44.1	432.1
32.5	6.793	61.454	17.088	0.000	14.422	0.243	31.510	43.5	425.9
33.5	7.101	61.974	17.223	0.000	14.449	0.253	31.672	43.8	429.0
34.5	7.171	61.716	17.371	0.000	14.572	0.270	31.943	44.1	432.1
35.5	7.046	61.250	17.102	0.000	14.356	0.246	31.458	43.5	426.3
36.5	6.947	61.015	17.293	0.000	14.545	0.200	31.838	43.9	430.1
37.5	6.621	61.092	16.870	0.000	14.160	0.257	31.030	42.8	419.7
38.5	6.692	61.793	17.033	0.000	14.297	0.185	31.330	43.2	423.1
39.5	6.744	61.868	16.939	0.000	14.206	0.242	31.145	43.0	431.4
40.5	6.512	62.036	16.972	0.000	14.229	0.251	31.201	43.0	431.2
41.5	6.488	62.767	16.563	0.000	13.969	0.240	30.505	42.2	413.0
42.5	6.416	62.807	16.596	0.000	13.222	0.959	29.818	41.6	407.4
43.5	6.423	63.292	16.263	0.000	13.795	0.227	30.058	41.6	407.5

EXAMPLE 8

TABLE 3

ACTIVITY OF A METATHESIS CATALYST

L3

Mar 29-30, 1990

Dimethylsilylene bis(cyclohexane diolato)wolfram

SiO₂ PQ cs-1231 0.6-1.6 mm

0.5425

310

183.85

1.4

400

N₂ ca. 10 l/h 600°C 1 h

1-6

No. of run:

Date:

PRECURSOR:

Carrier:

Mass of catalyst (g):

Area of catalyst (m²/g):

Molar mass of metal (g/mol):

Content of metal (%):

Temperature (°C):

Activation:

Propylene flow (l/h):

Time (h)	Ethylene (%)	Propylene (%)	Trans-2-butene (%)	1-butene (%)	Cis-2-butene (%)	Others (%)	Butenes (%)	Propylene conversion (%)	Activity (g/gh)	Notes
0.0	12.598	49.667	17.466	3.150	12.732	4.407	33.328	50.2	91.3	propylene 1.0 l/h
1.0	6.436	58.076	18.076	0.000	15.182	2.230	33.258	46.2	336.6	propylene 4.0 l/h
2.5	10.345	56.415	18.114	0.368	14.361	0.397	32.843	46.6	339.5	
3.5	7.526	53.699	21.545	0.000	16.867	0.363	38.412	51.8	377.0	
19.0	10.712	53.494	19.494	0.516	15.124	0.540	35.134	49.6	361.1	
20.0	10.041	56.116	18.476	0.415	14.531	0.421	33.422	47.2	343.7	
20.5	7.759	53.112	21.451	0.000	17.001	0.677	38.452	52.1	379.2	
21.5	6.335	55.258	21.064	0.000	16.707	0.636	37.771	50.6	368.7	
22.5	5.283	62.775	17.421	0.000	14.371	0.150	31.792	43.2	471.7	propylene 6.0 l/h
23.5	6.543	60.468	18.108	0.000	14.678	0.203	32.786	44.9	490.0	
24.0	9.026	62.826	15.344	0.000	12.627	0.117	27.971	40.0	437.5	
25.0	6.449	60.353	18.183	0.000	14.825	0.190	33.008	45.1	492.4	
26.0	6.273	61.226	17.784	0.000	14.542	0.175	32.326	44.2	482.9	

EXAMPLE 9

TABLE 4

ACTIVITY OF A METATHESIS CATALYST

Micro 1

Code of run:

WOC14

Date:

Apr 18-20, 1990

PRECURSOR:

W(O)C14

Carrier:

SiO₂ PQ cs-1231 0.6-1.6 mm

Mass of catalyst before run (g):

0.5302

after run (g)

0.3014

Content of metal before run (%):

2.3

after run (%):

2.2

Activation:

air ca 10 l/h 600°C 2 h W2 ca. 10 l/h 400°C 1.5 h

Temperature (°C)

400

Propylene flow (l/h):

1-6

Time (h)	Ethylene (%)	Propylene (%)	Trans-2-butene (%)	1-butene (%)	Cis-2-butene (%)	Butenes (%)	Others (%)	Propylene conversion (%)	Activity (g/gh)	Notes
1.0	3.196	86.581	4.883	0.590	4.674	10.147	0.076	15.0	31.2	propylene 1.0 l/h
2.0	3.086	78.327	7.352	0.659	3.451	11.462	7.125	18.0	37.5	
3.0	4.627	77.705	8.788	0.736	8.504	18.028	0.000	25.8	53.8	
4.0	4.323	75.581	9.936	0.816	9.344	20.096	0.000	28.5	59.5	
5.0	4.313	74.458	10.519	0.721	9.989	21.229	0.000	30.0	62.5	
6.0	4.471	73.174	10.975	0.714	10.396	22.085	0.000	31.2	65.0	
7.0	4.900	72.095	11.523	0.796	10.687	23.006	0.000	32.4	67.5	
8.0	5.082	71.506	11.694	0.673	11.046	23.413	0.000	32.9	68.7	
9.0	5.151	70.984	11.931	0.648	11.286	23.865	0.000	33.5	69.9	
10.0	5.234	70.247	12.292	0.632	11.595	24.519	0.000	34.4	71.7	
11.0	5.391	69.997	12.379	0.608	11.625	24.612	0.000	34.5	72.0	
12.0	5.683	69.477	12.505	0.598	11.737	24.840	0.000	34.9	72.8	
13.0	5.633	68.700	12.998	0.715	11.954	25.667	0.000	35.9	74.9	
14.0	5.794	68.688	12.884	0.576	12.058	25.518	0.000	35.8	74.6	
15.5	5.652	68.269	13.270	0.694	11.115	26.079	0.000	36.4	76.0	

TABLE 4 (continues)

16.5	6.011	68.169	13.069	0.559	12.192	25.820	0.000	36.2	75.6	150.3
17.5	5.969	67.759	13.371	0.655	12.246	26.272	0.000	36.8	76.7	153.5
18.5	5.981	67.889	13.261	0.543	12.345	26.129	0.000	36.6	76.3	150.4
19.5	5.947	67.879	13.298	0.527	12.349	26.174	0.000	36.6	76.4	148.9
20.5	2.472	85.064	6.129	0.000	6.334	12.463	0.000	18.0	150.3	propylene 4.0 l/h
21.5	2.610	85.665	6.212	0.000	6.514	12.726	0.000	18.4	153.5	
22.5	2.792	84.778	6.076	0.000	6.334	12.430	0.000	18.0	150.4	
23.5	2.757	84.937	6.073	0.000	6.233	12.306	0.000	17.9	148.9	propylene 6.0 l/h
24.5	1.941	87.884	4.923	0.000	5.252	10.175	0.000	14.8	185.2	
25.5	2.068	87.968	4.836	0.000	5.129	9.965	0.000	14.5	181.8	
26.5	2.044	88.475	4.592	0.000	4.889	9.481	0.000	13.8	173.3	
27.5	4.639	74.452	10.445	0.513	9.952	20.910	0.000	29.6	61.8	propylene 1.0 l/h
28.5	5.275	71.696	11.784	0.000	11.244	23.028	0.000	32.5	67.8	
29.5	5.573	70.538	12.366	0.000	11.522	23.888	0.000	33.7	70.3	
30.5	5.796	70.116	12.388	0.000	11.700	24.088	0.000	34.0	70.9	
31.5	5.737	69.872	12.525	0.000	11.865	24.390	0.000	34.4	71.7	
32.5	5.755	69.650	12.631	0.000	11.964	24.595	0.000	34.6	72.2	
33.5	5.751	69.383	12.891	0.000	11.975	24.866	0.000	35.0	72.9	
34.5	5.839	69.325	12.746	0.000	12.090	24.836	0.000	35.0	72.9	
35.5	5.783	69.297	12.809	0.000	12.111	24.920	0.000	35.0	73.1	
36.5	5.626	69.041	13.014	0.000	12.319	25.333	0.000	35.5	74.0	
37.5	6.069	68.330	13.304	0.000	12.297	25.601	0.000	36.0	75.0	
38.5	5.885	68.303	13.408	0.000	12.404	25.812	0.000	36.2	75.5	
39.5	6.112	68.219	13.220	0.000	12.448	25.668	0.000	36.1	75.2	
40.5	6.020	68.177	13.407	0.000	12.396	25.903	0.000	36.2	75.5	
41.5	6.025	68.316	13.263	0.000	12.423	25.686	0.000	36.1	75.2	
42.5	5.921	68.312	13.287	0.000	12.460	25.767	0.000	36.1	75.4	

EXAMPLE 10

TABLE 5

ACTIVITY OF A METATHESIS CATALYST

No. of run: Test 15
 Date: Jul 31-Aug 3, 1989
 PRECURSOR: $(\text{NH}_4)_2\text{WO}_4$
 Carrier: Silica P0 cs-1231 0.6-1.6 mm
 Mass of unused catalyst (g): 0.3782
 Mass of catalyst used (g): 0.3664
 Metal content before run (%): 5.8
 Metal content after run (%): 6.3
 Activation: air ca. 10 l/h 600°C 1.5 h, N2 10 l/h 600°C 0.5 h
 Temperature (°C): 400
 Propylene flow (l/h): 0.09-4.09

Time (h)	Ethylene (%)	Propylene (%)	Trans-2-butene (%)	1-butene (%)	Cis-2-butene (%)	Others (%)	Butenes (%)	Propylene conversion (%)	Activity (g/g h)	Notes
1.0	4.378	76.505	6.668	1.891	5.505	5.503	14.064	21.6	14.2	400°C 1.1 l/h
2.0	6.111	73.233	9.204	2.322	7.628	1.502	19.154	28.2	18.6	
4.0	7.635	66.508	11.827	2.563	9.650	1.817	25.040	35.2	23.2	
7.0	8.939	61.344	13.676	3.210	10.795	2.036	27.681	40.4	26.6	
8.0	9.015	61.178	13.850	3.004	10.910	2.043	27.764	40.5	26.7	
11.0	9.151	60.485	14.429	2.686	11.417	1.832	28.532	41.4	27.3	
12.0	9.034	60.840	14.450	2.389	11.498	1.789	28.337	41.1	27.1	
16.0	9.361	59.583	15.055	2.339	11.879	1.783	29.273	42.4	28.0	
17.0	9.334	59.596	15.081	2.302	11.922	1.765	29.305	42.4	28.0	
18.0	9.529	59.902	15.304	2.499	11.959	1.807	29.762	43.1	28.4	
19.0	9.455	59.027	15.305	2.351	12.058	1.804	29.714	43.0	28.4	
20.0	9.412	59.227	15.297	2.321	12.044	1.699	29.622	42.9	28.3	
21.0	9.535	59.134	15.672	2.176	12.290	1.193	30.138	43.3	28.6	
22.0	11.956	59.594	15.110	3.487	10.751	2.102	29.348	44.8	13.6	400°C 0.52 l/h
23.0	12.006	56.245	14.816	3.896	10.524	2.515	29.234	43.8	13.6	
24.0	11.970	56.583	14.565	3.956	10.375	2.551	28.896	43.4	13.5	
27.5	12.574	57.121	13.803	4.160	9.797	2.545	27.760	42.2	13.1	
28.5	9.341	59.644	14.912	2.526	11.846	1.731	29.284	42.4	28.0	400°C 1.1 l/h

Claims

1. A catalyst for use in the metathesis reactions of olefines, characterized in that it comprises an after-treated wolfram complex, which contains diol ligands and hydrocarbon ligands, which latter are benzenes substituted with a lower alkyl group.
2. A catalyst according to Claim 1, characterized in that the substituted benzene is mesitylene.
3. A catalyst according to Claim 1 or 2, characterized in that the structure of the precursor of the catalyst is $\text{W}(\text{ArCH}_2)_2(\text{diol})_2$, in which ArCH_2 is mesitylene and diol is 1, 2-cyclohexane diol or picanol.
4. A catalyst according to any of the Claims 1-3, characterized in that the catalyst precursor is impregnated in silica and calcined.

5. A method for preparing a heterogenous catalyst for use in the metathesis reaction of olefines, characterized in that
- a) a complex between an inorganic wolfram salt and a diol is formed,
 - b) the complex obtained is caused to react with a benzyl anion or a benzyl anion substituted with a lower alkyl group for obtaining a wolfram complex containing diol ligands and benzyl ligands or benzyl ligands substituted with a lower alkyl group, and
 - c) the wolfram complex obtained is impregnated into a carrier and calcined.
6. A method according to Claim 5, characterized in that the inorganic wolfram salt is a wolfram halide, preferably a wolfram chloride WCl_6 .
7. A method according to Claim 5 or 6, characterized in that the diol is picanol or 1, 2-cyclohexane diol.
8. A method according to any of Claims 5-7, characterized in that the carrier is a silica.
9. A method according to any of the Claims 5-8, characterized in that the complex of the wolfram salt and the diol is treated with a halide of a benzene substituted with a lower alkyl group, preferably with a bromide and a magnesium metal.
10. A method according to any of the Claims 5-9, characterized in that the impregnation is performed from an inert solvent into a carrier, which is preferably a silica.
11. A method according to any of the Claims 5-10, characterized in that the calcination with an inert gas, preferably nitrogen, is performed at a temperature of 400-800°C.
12. A metathesis process for the conversion of olefines, wherein a catalyst comprising a wolfram compound converts the olefine into olefines having a different molecular weight, characterized in that said heterogenous catalyst comprises an after-treated wolfram complex, which contains diol ligands and benzyl ligands substituted with a lower alkyl group.
13. A process according to Claim 12, characterized in that the olefine comprises one or more olefines, e.g. an ethene or a 2-butene, for preparing a propylene.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 6733

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
A	US-A-4 818 442 (VANDERVEEN ET AL) ---		B01J31/12 C07C6/04 C07C11/06
D,A	EP-A-0 129 474 (SOCIETE NATIONALE ELF AQUITAINE) ---		
D,A	US-A-3 956 178 (GRECO ET AL) -----		
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
			B01J C07C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 03 NOVEMBER 1992	Examiner LO CONTE C.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (03.92) (P0401)